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13. ABSTRACT (Maximum 200 words)

The facile thermolysis of $[Cl_2GaP(SiMe_3)_2]_2$ to eliminate Me_3SiX and yield nanocrystalline GaP has been studied *via* thermal gravimetric analysis (TGA) and it has been found that the Me_3SiCl is eliminated in a step-wise manner. Also, the new ternary single-source precursor $[Ga_2(As,P)Cl_3]_n$ has been synthesized and thermolyzed to yield the ternary III-V $GaAs_xP_y$. In addition, nanocrystalline GaAs and GaP, prepared by the Kher/Wells low temperature solution phase method, have been studied by transmission electron microscopy (TEM) and, in the TEM's of both, the lattice fringes of nanocrystalline material are clearly evident. Using a host of analytical techniques, it has been shown that the GaAs has crystalline regions of 12 +/- 2 nm. In addition, efforts in immobilization of particles have involved all binary permutations of In and Ga phosphides and arsenides. The materials have been cast onto electrode surfaces from volatile solvents to give uniform deposits. Dispersions can also be created in the presence of monomers which are subseqently electropolymerized to prepare composite films. In an STM plot of InAs immobilizeded in a poly(pyrrole) film, the nanocrystals appear as yellow dots embedded in the brown film, indicating that they extend above the film, and/or have a higher conductivity than the polymer.

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ARTICLES/BOOKS PUBLISHED RELATED TO AFOREMENTIONED CONTRACT/GRANT

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NOTE 2: Only include publications in peer reviewed professional journals and refereed book chapters. Do not include: Abstracts, "Scientific American" type articles, or articles that are not primary reports of new data, and articles submitted or accepted for publication, but with a publication date outside the stated time frame.

JOURNAL or BOOK (Circle one) Publisher: American Chemical Society

Journal/Book Name: *Chemistry of Materials*

Journal/Book Author: Aubuchon, S.R.; McPhail, A.T.; Wells, R.L.; Giambra, J.A.; and Bowser, J.R.

Subject Author: "Preparation, Characterization and Facile Thermolysis of $[X_2GaP(SiMe_3)_2]_2$ (X = Br, I) and $(Cl_3Ga_2P)_n$: New Precursors to Nanocrystalline Gallium Phosphide"

Journal Volume/Book Chapter: 6 Month Published: January Year Published: 1994

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JOURNAL or **BOOK** (Circle one)   **Publisher:** Pergamon Press

Journal/Book Name: *Polyhedron*

Journal/Book Author: Sir G. Wilkinson, Editor

Subject Title: "Synthesis and Molecular Structures of $R(Me_3CCH_2)_2In \bullet E(SiMe_3)_3$ ($R = Me_3CCH_2$, E = P or As; R = Me, E = P)"

Subject Author: Self, M.F.; McPhail, A.T.; Jones III, L.J.; and Wells, R.L.

Journal Volume/Book Chapter: 13   **Month Published:** February   **Year Published:** 1994
pp. 625-634.

JOURNAL or **BOOK** (Circle one)   **Publisher:** Materials Research Society

Journal/Book Name: *Materials Research Society Symposium Proceedings*

Journal/Book Author: Cammerata, R.C.; and Gonsalves, K.E.; Eds.

Subject Title: "A Low Temperature, Solution Phase Synthesis of III-V Semiconductor Nanocrystals"

Subject Author: Kher, S.S.; and Wells, R.L.

Journal Volume/Book Chapter: 351   **Month Published:** September   **Year Published:** 1994
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Awarding Organization: Department of Chemistry, Duke University

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Research Highlights - For the Period 1 October 1993 through 30 September 1994

R. L. Wells and L. A. Coury,

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Explanatory Notes

Vugraph 1 - Introduction

Recent research in Professor Wells' laboratories at Duke University has demonstrated the utility of silyl cleavage by showing that reactions between $GaCl_3$ and $As(SiMe_3)_3$ or $P(SiMe_3)_3$ in hydrocarbon solvents yield nanocrystalline GaAs or new cyclic precursors which can be thermally decomposed to yield nanocrystalline GaP (vu 1, eq 1). Two other research groups have utilized the silyl cleavage reaction to synthesize GaAs nanocrystals in quinoline. In addition, Uchida *et al.* reported the synthesis of GaAs and InAs nanocrystals from $Ga(acac)_3$ and $In(acac)_3$, respectively, by reactions with $As(SiMe_3)_3$, however, formation of by-products or the fate of the acetylacetonate ligands were not reported (vu 1, eq 2). In addition, it has been demonstrated by the Wells group that $GaCl_3$ and $As(SiMe_3)_3$ or $P(SiMe_3)_3$ mixed in a 2:1 ratio react to yield in each case a stable substance having the empirical formula Ga_2ECl_3 (E = As or P) (vu 1, eq 3). These substances eliminate $GaCl_3$ at elevated temperatures to give nanocrystalline GaAs and GaP, respectively (vu 1, eq 3).

Recently Kaner and co-workers reported a general method involving solid state metathesis (SSM) to synthesize binary III-V semiconductors by reacting sodium pnictides with Group III trihalides either in bombs or sealed glass ampules at high temperatures (vu 1, eqs 4 and 5) . These exothermic reactions generate enough heat to melt the sodium halide product and, therefore, SSM reactions yield polycrystalline III-V semiconductors often contaminated with starting materials and by-products. It has also been reported that the III-V materials produced by this method contain considerable amounts of non-removable halide inclusions and the rapid exothermic SSM reactions introduce high defect concentration and lattice strain in resulting materials.

Vugraph 2 - Research Highlight One

The previously mentioned (see above, sentence 1) new cyclic compounds with Ga-P containing cores and exocyclic halogen ligands on the metal centers undergo facile thermolysis to eliminate Me_3SiX and yield nanocrystalline GaP (vu 2, eq). This thermolysis can be studied *via* thermal gravimetric analysis (TGA). The TGA of the chlorine-containing cyclic compound, which is shown on viewgraph 2, clearly exhibits separate transitions, corresponding to a stepwise elimination of Me_3SiCl.

Viewgraph 3 - Research Highlight Two

As noted on the introductory viewgraph, Wells and co-workers has reported the synthesis of single-source precursors of the general formula $(Ga_2ECl_3)_n$ which can be thermolyzed to yield nanocrystalline binary semiconductor materials. As illustrated by equations 1 and 2 on vugraph 3, they have now applied this methodology to the synthesis of a single-source precursor to a ternary III-V, namely, gallium arsenide phosphide. The figure shown on viewgraph 3 compares the diffraction patterns of

GaAs, GaP and GaA_xP_y, all prepared using the same methodology/technique. The ternary material exhibits hybrid characteristics of the two binaries, with d-spacing values directly between those of GaAs and GaP. This is conclusive evidence for a semiconductor solid-solution, according to Vegard's Law.

Viewgraph 4 - Research Highlight Three

Kher and Wells have reported the development of a new, low temperature solution phase synthesis of nanocrystalline III-V semiconductors. Their methodology involves in situ formation of the sodium/potassium pnictide, followed by reaction with the metal halide to form the semiconductor quantum dots (see vu 4, eqs 1 and 2). These materials have been studied by transmission electron microscopy (TEM). In the TEM's shown on viewgraph 4, the lattice fringes of nanocrystalline GaAs and GaP are clearly evident.

Viewgraph 5 - Research Highlight Four

Co-PI Coury and coworkers have conducted the first characterization of nanocrystalline GaAs prepared by the solution metathesis reaction of Kher and Wells. Using a host of analytical techniques, they have shown that this material has crystalline regions of 12 +/- 2 nm. The particles themselves are of similar total size, and are roughly spherical in shape. The as-prepared material is relatively free of surface oxides, although prolonged exposure to water results in the formation of soluble, acidic arsenic compounds, detectable by electrochemical techniques. High resolution electron microscopy showed that aggregates of the particles can be dispersed by sonication, but that the nanocrystalline lattices remain unaffected by ultrasound. The particles appear to be relatively conductive, since they obtained stable images by scanning tunneling microscopy (STM) using similar bias voltages to those employed for imaging bulk GaAs wafers. Finally, very recent solid-state luminescence measurements have revealed clear evidence for quantum confinement through blue-shifted emission maxima. Our efforts in immobilization of the particles have involved all binary permutations of In and Ga phosphides and arsenides. These materials can be cast onto electrode surfaces from volatile solvents to give uniform deposits. Dispersions can also be created in the presence of monomers which are subsequently electropolymerized to prepare composite films. Image A on viewgraph 5 shows the STM of a conductive poly(pyrrole) film grown on a Pt electrode. The image is relatively featureless, indicating a smooth, uniform film. By comparison, InAs crystals deposited from a methanol suspension are shown in image B on a scale of 400 x 400 nm. The particles are easily visible and are of uniform size, as seen in the profilometer trace (top). Image C shows the STM of InAs immobilized in a poly(pyrrole) film. In this plot, the nanocrystals appear as yellow dots embedded in the brown film, indicating that they extend above the film, and/or have a higher conductivity than the polymer.

Introduction

Syntheses of III-V Nanocrystals

$$\underset{E = P,\ As}{GaCl_3 + E(SiMe_3)_3} \longrightarrow \underset{\text{nanocrystalline}}{GaE} + 3Me_3SiCl \qquad (1)$$

Wells and co-workers (a) *Chem. Mater.* 1989, *1*, 4; (b) *Mater. Res. Soc. Symp. Proc.* 1989, *131*, 45; (c) *Chem. Mater.* 1991, *3*, 382; (d) *Organometallics* 1993, *12*, 2832; (e) *Chem. Mater.* 1994, *6*, 82.

Alivisatos and co-workers *J. Am. Chem. Soc.* 1990, *112*, 9438.

Uchida et al. *J. Phys. Chem.* 1991, *95*, 5382.

$$\underset{M = Ga,\ In}{M(acac)_3 + As(SiMe_3)_3} \longrightarrow \underset{\text{nanocrystalline}}{MAs} \qquad (2)$$

Uchida et al. (a) *J. Phys. Chem.* 1992, *96*, 1156; (b) *Chem. Mater.* 1993, *5*, 716

$$\underset{E = P,\ As}{2\,GaCl_3 + E(SiMe_3)_3} \xrightarrow{-3\,Me_3SiCl} 1/n(Ga_2ECl_3)_n \xrightarrow[-\,GaCl_3]{\Delta} \underset{\text{nanocrystalline}}{GaE} \qquad (3)$$

Wells, R. L.; Self, M. F.; McPhail, A. T.; Aubuchon, S. R.; Woudenberg, R. C.; Jasinski, J. P. *Organometallics* 1993, *12*, 2832.

Aubuchon, S. R.; McPhail, A. T.; Wells, R. L.; Giambra, J. A.; Bowser, J. R. *Chem. Mater.* 1994, *6*, 82.

Solid-State Synthesis of Polycrystalline III-V Semiconductors

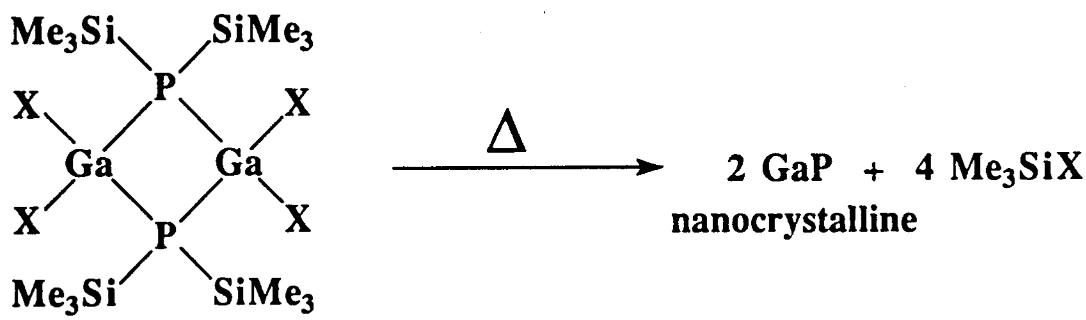
$$\underset{E = P,\ As,\ Sb}{3Na + E} \longrightarrow Na_3E \qquad (4)$$

$$Na_3E + MX_3 \xrightarrow[8\text{-}42\ h]{\text{Bomb ignition or } 550\text{-}990\ ^{\circ}C} \underset{\text{polycrystalline}}{ME} + 3NaX \qquad (5)$$

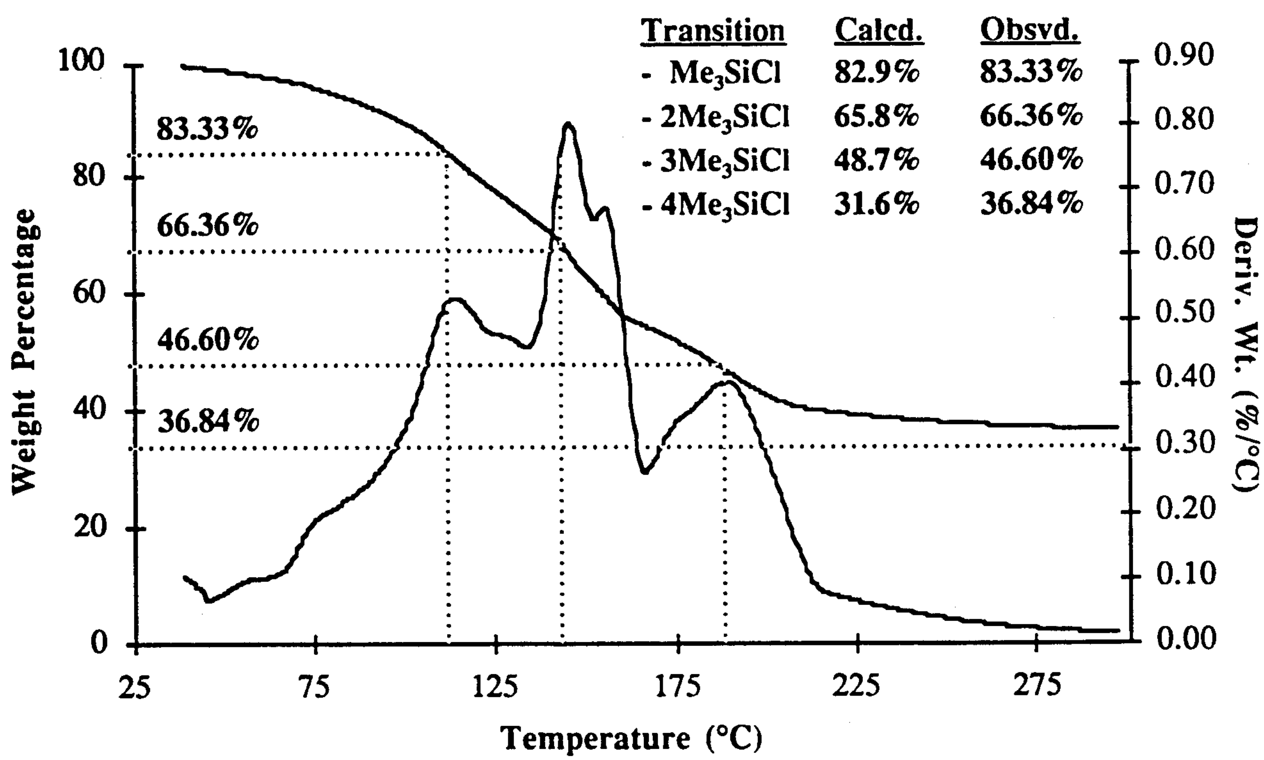
$M = Al$, $X = I$
$M = Ga$, $X = F, Cl, I$
$M = In$, $X = F, I$

Kaner and co-workers (a) *Chem. Mater.* 1992, *4*, 9 (b) *Mater. Res. Soc. Symp. Proc.* 1992, *271*, 169; (c) *Science* 1992, *255*, 1093; (d) *Inorg. Chem.* 1993, *32*, 2745.

Research Highlight: Decomposition Studies



X = Cl, Br, I



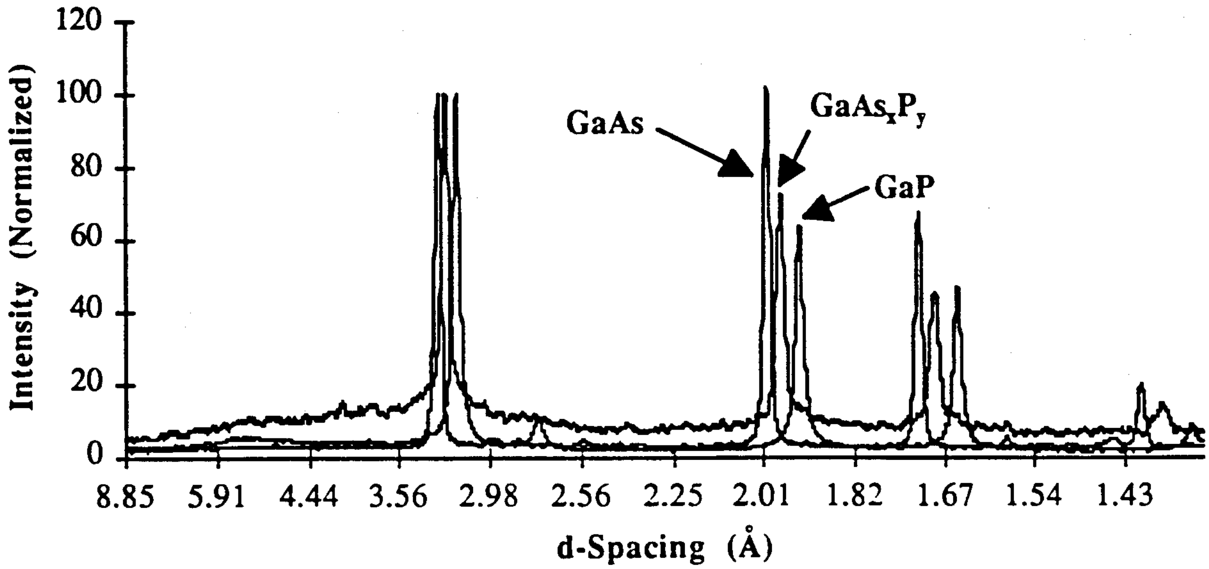
TGA of $[Cl_2GaP(SiMe_3)_2]_2$

Research Highlight: New Ternary III-V Single-Source Precursor

$$2GaCl_3 + 0.5As(SiMe_3)_3 + 0.5P(SiMe_3)_3 \xrightarrow{-3\,Me_3SiCl} 1/n[Ga_2(As,P)Cl_3]_n \quad (1)$$

$$1/n[Ga_2(As,P)Cl_3]_n \xrightarrow[\Delta]{-\,GaCl_3} GaAs_xP_y \quad (2)$$

$$x = 0.6,\ 0.6<y<0.9$$



XRD Powder Patterns

Research Highlight: New, Low Temperature Solution Phase Synthesis of III-V Quantum Dots

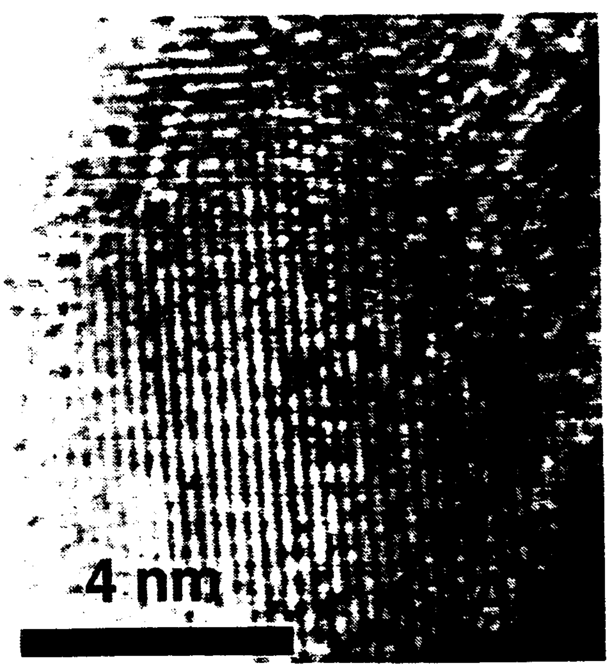
$$3(\text{Na/K}) + \text{E} \xrightarrow[\text{aromatic solvent}]{\text{reflux}} (\text{Na/K})_3\text{E} \qquad (1)$$

$\text{E} = \text{P, As, Sb}$

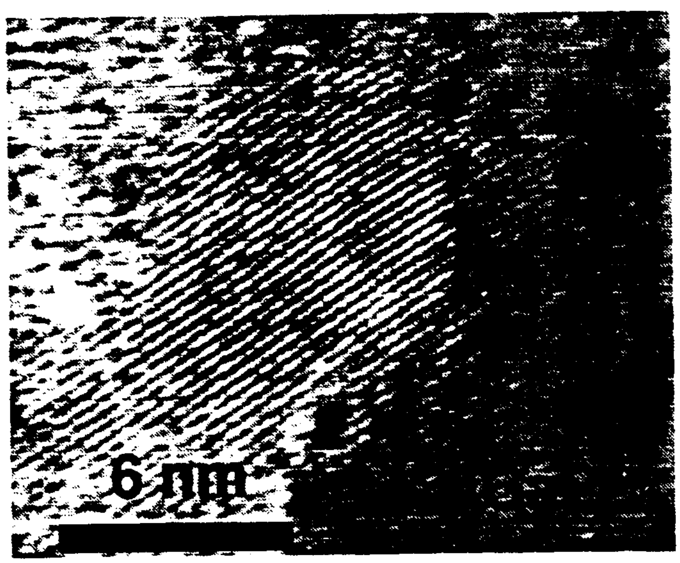
$$\underset{\substack{\text{in}\\\text{aromatic}\\\text{solvent}}}{(\text{Na/K})_3\text{E}} + \underset{\substack{\text{in}\\\text{glyme}\\\text{solvent}}}{\text{MX}_3} \xrightarrow{\text{reflux}} \underset{\text{nanocrystalline}}{\text{ME}} + 3\,(\text{Na/K})\text{X} \qquad (2)$$

$\text{M} = \text{Ga}, \text{X} = \text{Cl, I}$
$\text{M} = \text{In}, \text{X} = \text{I, Cl, Br}$

Kher, S. S.; Wells, R. L. *Mater Res. Symp. Proc.* 1994, *351*, 293.
Kher, S. S.; Wells, R. L. *Chem. Mater.* 1994, *in press.*
Kher, S. S.; Wells, R. L. *U.S. Patent Application Serial No. 08/189,232,* filed Jan. 31, 1994, *pending.*



TEM



TEM

Research Highlight:
Characterization and Immobilization

- Rigorous, multi-technique characterization of GaAs Quantum Dots
  - X-Ray Diffraction (average crystallite size)
  - TEM & SEM (extent of aggregation; lattice planes)
  - Multi-Point BET (surface area and particle shape)
  - STM (nanoscopic conductivity and morphology)
  - Photoluminescence (band gap; quantum confinement)
  - Voltammetry (extent of surface oxidation)
  - XPS (surface elemental composition)

- Immobilization of GaAs, GaP, InP and InAs
  - solvent casting on electrode surfaces
  - immobilization in conducting organic films of poly(pyrrole)

STM Images:

A. poly(pyrrole)

B. InAs on Pt

C. InAs in poly(pyrrole)